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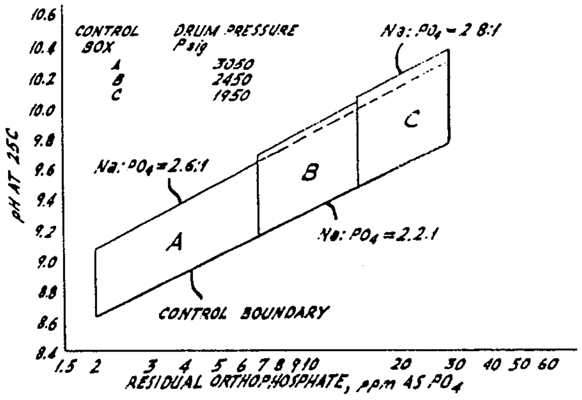
㊴ **Corrosion inhibitor method for the treatment for boiler water.**

㊷ There is disclosed a coordinated phosphate/pH corrosion control method for the treatment of boiler water, in which said treatment in supplemented with an alpha amine-neutralized organic acid. An alpha amine is one which has a distribution ratio of 0.01 or greater and a pK_b of 8.0 or less.



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DESCRIPTION

CORROSION INHIBITOR METHOD FOR THE TREATMENT FOR BOILER WATER

Boilers using demineralized makeup water are known to be prone to caustic attack. High pressure boilers are particularly susceptible to this type of metal corrosion.

The inside surfaces of the boiler are typically protected with magnetite. Hydroxide ion, being the predominant anion in high purity boiler water, can dissolve the magnetite when highly concentrated. Even though high purity water is being used, caustic can nonetheless become highly concentrated, primarily due to the presence of iron oxide deposits on radiant wall tubes. While the bulk water may contain only 5-10 ppm of caustic, it is quite possible to have localized caustic concentrations of up to 100,000 ppm. The iron oxide deposits are extremely porous so that water is drawn thereinto. Due to heat being applied from beneath, steam is generated and passes out of the porous deposit, while fresh water is again drawn thereinto. The result is the noted high concentrations of caustic which must be dealt with if the boiler is to properly be protected.

A widely used method for controlling caustic corrosion in boilers using demineralized (high purity) makeup water, particularly in high pressure boilers, is the coordinated phosphate/pH control treatment. This method of treatment is detailed in an article by George Gibson entitled "The Basics of Phosphate-pH Boiler Water Treatment", Power Engineering, February, 1978, p. 66, which article is incorporated herein by reference to the extent necessary to complete this disclosure. In any event, portions are excerpted below for purposes of explanation.

The coordinated phosphate/pH corrosion control treatment is based on two principles: first, that sodium phosphates are a pH buffer; and second, that disodium hydrogen phosphate converts potentially corrosive caustic into relatively harmless trisodium phosphate according to the following equation:

$$\underset{\text{disodium hydrogen phosphate}}{Na_2HPO_4} + \underset{\text{caustic}}{NaOH} \longrightarrow \underset{\text{trisodium phosphate}}{Na_3PO_4} + \underset{\text{water}}{H_2O} \quad (1)$$

Accordingly, general corrosion is prevented through the control of boiler water pH, and adherent deposits with concomitant caustic corrosion are prevented by maintaining a disodium hydrogen phosphate residual in the boiler water to react with caustic according to equation (1).

The program is implemented with a control chart such as in Figure 1. Disodium hydrogen phosphate is present if the coordinate of pH and phosphate lies within the control boundary.

Many sodium phosphates are used in boiler water treatment. Of these, orthophosphates are preferred. Complex phosphates, in the form of polymer chains, break down into orthophosphates at boiler water temperatures by a process known as reversion. The orthophosphates are monosodium dihydrogen phosphate (MSP), disodium hydrogen phosphate (DSP) and trisodium phosphate (TSP).

Orthophosphates can be identified by name, formula or sodium-to-phosphate ratio which can be expressed with the notation "$Na:PO_4$", read as sodium-to-phosphate ratio.

Monosodium dihydrogen phosphate has one mole of sodium per mole of phosphate. Therefore, the sodium-to-phosphate ratio is one-to-one ($Na:PO_4 = 1:1$). Disodium hydrogen phosphate, with two moles of sodium per mole of phosphate, has a $Na:PO_4 = 2:1$, and trisodium phosphate has a $Na:PO_4 = 3:1$.

Sodium-to-phosphate ratios are useful to describe mixtures of phosphates in solution. For example, solutions of DSP and TSP have a $Na:PO_4$ between 2:1 and 3:1. The $Na:PO_4$ is fairly proportional to the mix ratio. For instance, a solution of half DSP and half TSP has a ratio of about 2.5:1 (it is actually 2.46:1 because DSP and TSP have different molecular weights).

Figure 2 shows the relation between solution pH and phosphate concentration for various sodium-to-phosphate molar ratios. Examination of the figure reveals pH increases with increasing $Na:PO_4$ (at equal phosphate concentrations). Accordingly, solution pH and phosphate concentration identify phosphate form, it being kept in mind that disodium hydrogen phosphate is the species which neutralizes caustic according to equation (1).

A trisodium phosphate solution exists if the phosphate/pH coordinate falls on the Na:PO_4 = 3:1 line; disodium hydrogen phosphate solution if the coordinate falls on the 2:1 line; and a mixture of DSP and TSP if the coordinate falls between the 2:1 and 3:1 lines. As the coordinate approaches the 3:1 line, there is more and more TSP and less and less DSP in the solution.

The solution is a mixture of TSP and caustic if the coordinate falls above the 3:1 line. In this "free caustic" region there is no DSP to tie up the caustic.

It is seen that the phosphate/pH coordinate must be below the Na:PO_4 = 3:1 line to ensure that there is DSP in solution to tie up the caustic. The further the phosphate/pH coordinate is kept below the line the greater the caustic-absorbing capacity of the water and the less chance of drifting into the region above the 3:1 line.

Figure 2 is based on pure sodium phosphate solution. The pure solution theory can be used with impure boiler water because the concentration of other species is low and their solubility high. Complex chemistry is avoided by using pH as a variable. It is desirable to keep the Na:PO_4 between 2.8:1 and 2.2:1. The phosphate-pH control chart, Figure 1, is a refinement of Figure 2 with a control boundary in the appropriate range to prevent caustic corrosion. The control chart is the heart of phosphate-pH control.

There has been some confusion in applying sodium-to-phosphate ratios. The Na:PO_4 used in phosphate-pH control is determined only from boiler water pH and phosphate concentration, not by measuring sodium and phosphate concentrations of the boiler water.

This information can be used to make a phosphate-pH control chart by first setting phosphate limits. Maximum allowable phosphate decreases with increasing boiler pressure because of carryover and phosphate "hideout." The latter term, incidentally, refers to the phenomenon of diminishing boiler water phosphate levels with increased firing rate (everything else held constant) and the reappearance of boiler water phosphate level when the firing rate is reduced. Hideout phosphate is believed to be caused by precipitating the phosphates under high heat flux conditions.

Individual plants have set their own phosphate limits, based on what works for them and on results at similar installations. The limits chosen for the control chart shown in Figure 1 are consistent with industry practice and have proved to be satisfactory in practical applications.

Note that the residual phosphate limits contained in the control chart (Figure 1) are the maximum levels recommended for satisfactory boiler operation. Whatever the allowable residual phosphate concentration, it is prudent to operate with as little phosphate as practicable.

There should be an upper Na:PO_4 limit of 2.85:1 to prevent caustic corrosion and a lower Na:PO_4 limit of 2.13:1 to prevent acid attack. But, it would be prudent to include a safety factor into these numbers, which safety factor depends on individual boiler characteristics and system water tightness. Lower pressure boilers have less trouble with caustic corrosion than higher pressure boilers and generally can be run with Na:PO_4 close to the 2.85:1 line. Of course, if caustic corrosion is occurring, a lower maximum limit should be set for the boilers involved. High pressure boilers tend to be more susceptible to caustic corrosion, and a maximum Na:PO_4 line of 2.6:1 usually is chosen. This has proved to be an effective limit.

It should be understood from the foregoing that the coordinated phosphate/pH control treatment consists primarily of two basic steps as follows:

(1) maintenance of an appropriate level of residual orthophosphate in the boiler water; and

(2) maintenance of the proper Na:PO_4 ratio in the water.

The residual orthophosphate level will depend on such known factors as the nature and severity of the problem and boiler pressure. Since it is considered best to operate with as little phosphate as possible, amounts as low as about 1 ppm could be used, with about 2 ppm being the preferred minimum. While amounts as high as about 50 ppm residual orthophosphate could be used, about 30 ppm is the preferred maximum.

While the coordinated phosphate/pH corrosion control treatment is widely used, it is not without its drawbacks and limitations. Often, it is desirable to supplement the treatment with additional corrosion inhibitor; however, this is not always practicable. It has been customary for many years to use the sodium salt of a polymeric dispersant, such as sodium polymethacrylate, as the supplement. When the sodium salt form is used, the Na:PO_4 in the boiler water is often significantly altered and the solids level of the boiler water rises. If the Na:PO_4 is allowed to rise over the 3:1 line of Figure 2, caustic attack again becomes a problem, and, particularly in high pressure boiler systems, increased solids levels can lead to undesirable foaming in the water. Thus, the use of supplemental treatment has been severely limited. In fact, when the Na:PO_4 is near the control limit, the supplemental treatment has been completely omitted.

The present invention relates to an improvement in the coordinated phosphate/pH corrosion control treatment for boiler water. According to the present invention, a supplemental corrosion inhibitor is provided which neither significantly alters the sodium burden of the boiler nor significantly increases the solids level therein.

The present invention is drawn to the use, in conjunction with a coordinated phosphate/pH corrosion control treatment, of an aqueous solution of an organic acid dispersant which has been neutralized with any one of a class of specific amines, hereinafter referred to as "alpha" amines. More specifically, according to the present invention, the organic acid dispersant is neutralized with a suitable amine (or NH_3) which is volatile under the conditions of the boiler water to be treated and has a basicity constant of 8.0 or less. A detailed description of how to determine suitable amines is presented below.

The invention offers certain advantages as follows:

(1) the sodium burden in the boiler is limited, thus limiting caustic gouging and other forms of boiler metal corrosion;

(2) advantage (1) is accomplished with volatile materials that do not concentrate in the boiler and, thereby, do not contribute to either corrosion or deposition processes; and

(3) the supplemental material will aid in corrosion control in both the boiler and in the steam distribution system (due to volatile neutralizing agents).

The utility of the present invention is considered to be greatest for those high pressure (above about 900-1200 psig) boiler systems experiencing difficulty in maintaining a $Na:PO_4$ less than 2.8:1. The use of a low sodium supplement under these conditions does not contribute to the sodium burden of the boiler, thereby simplifying the maintenance of a coordinated phosphate/pH control treatment, *i.e.*, supplemental feed to the boiler feedwater can be made without disrupting the sodium to phosphate ratio.

According to the present invention, a supplemental corrosion inhibitor is provided in which a volatile organic base has replaced caustic as a neutralizing agent. This resulting alkaline product is considered to be preferable to an acidic product. Furthermore, the volatile organic base finds utility as a condensate corrosion inhibitor, neutralizing carbonic acid at steam condensation sites.

The Organic Acid

Any reference hereinafter to the polymers used in accordance with the present invention is intended to include the polymers individually as well as any combination of homopolymer, copolymer and mixtures thereof. The term "polymeric acid" is intended to include any polymer containing acid functional group(s), as well as acid precursor compounds (e.g., anhydrides).

As already noted, the compounds which are considered to be useful in practicing the present invention are any of the well known organic acid dispersants, such as polymeric sulfonic acids, polymeric phosphonic acids, polymeric carboxylic acids and poly phosphonic acids.

Illustrative examples of polymeric carboxylic acids would be as follows:

polyacrylic acid
polymethacrylic acid
polymaleic anhydride
acrylic acid/hydroxypropylacrylate copolymer
sulfonated styrene/maleic anhydride copolymer
methylvinyl ether/maleic anhydride copolymer
acrylic acid/methacrylic acid copolymer

Illustrative examples of polymeric sulfonic acids would be as follows:

sulfonated polystyrene
polyvinylsulfuric acid
sulfonated styrene/maleic anhydride copolymer
polyvinylsulfonic acid
poly[2-acrylamido-2-methylpropanesulfonic acid]

Illustrative examples of poly phosphonic acids would be:

ethylenediamine tetra(methylene phosphonic acid)
1-hydroxyethylidene-1,1-diphosphonic acid
nitrilotri(methylene phosphonic acid)

These compounds are believed to be useful in boilers of up to about 1500 psig.

The polymeric phosphonic acids are believed to be suitable for use at pressures up to well above 1500 psig; however, few are presently commercially available. Illustrative examples of these compounds are polyvinyl phosphonic acid and its substituted analogs.

As is well known in the art, the amount of supplemental corrosion inhibitor would depend on such factors as the nature and severity of the problem to be treated and could vary over a wide range. The amount of organic acid could, accordingly, be as low as about 1 part polymer per million parts of boiler water (ppm). The preferred minimum is considered to be about 5 ppm. Based on economic considerations, the upper limit for the organic acid dosage is considered to be about 150 ppm; while 50 ppm represents the preferred maximum.

With respect to the polymeric organic acids, it is well known that molecular weight is not critical. In any event, a molecular weight of from about 1000 to about 200,000 is believed to be operable.

The Neutralizing Agent

Suitable amines for use as neutralizing agents in accordance with the present invention have already been described as alpha amines. The important properties of these amines are, first, that they are volatile under the operating conditions of the boiler and, second, that they have sufficient basicity to neutralize the organic acid dispersant. Defining the first property in terms of distribution ratio and the second in terms of basicity constant, pK_b, alpha amines are those having a distribution ratio of 0.01 or greater under the operating conditions of the boiler and a pK_b of 8.0 or less.

The distribution ratio, DR, is defined as the quantity of voltile amine found in the steam phase over the quantity found in the bulk fluid and is represented by:

$$DR = \frac{\text{ppm amine in steam}}{\text{ppm amine in blowdown}} \qquad (I)$$

The values for this ratio, of course, are easily obtained by drawing a condensed steam sample and a blowdown sample from the boiler and analyzing for respective amine contents.

The basicity constant is a well known comparison for basicities of amines in terms of their respective abilities to accept hydronium ion from water. Using the reaction:

$$RNH_2+H_2O \rightleftarrows RNH_3^+ + OH^-,$$

the basicity constant, pK_b, is defined by:

$$pK_b = -\log \frac{[RNH_3^+][OH^-]}{[RNH_2]} .$$

Each amine has its own pK_b, and, the lower the value, the stronger the base. As is well known to the artisan, tabulated values for pK_b's are readily obtainable from numerous chemical reference books. For example, a table of such values can be found in the "Handbook of Chemistry and Physics", The Chemical Rubber Co., 45th Edition (1964-1965), p. D-76.

Following is an exemplary list of alpha amines believed to be suitable for use in accordance with the present invention:

morpholine
aminomethylpropanol (AMP)
dimethylaminomethylpropanol (DMAMP)
cyclohexylamine
dimethylpropanolamine (DMPA)

diethylaminoethanol
N-hexylamine
methoxypropylamine (MPA)
benzylamine
ammonia
monoisopropanolamine
1,6 hexanediamine
1,3 diaminopropane
tributylamine
triethylamine
n-amylamine
n-methylmorpholine
N,N-dimethyl-1,3 propanediamine.

EXAMPLES

Determining Distribution Ratios

Example 1

A first series of tests were conducted to determine the DR's of various amines using a research boiler similar to the one schematically illustrated in Figure 3. Two fiberglass feed tanks were filled with a total of 600 liters of deionized water which was deaerated by nitrogen sparging for two hours. At the end of the deaeration period one tank was charged with 50 ppm amine, while the other was charged with various chemicals to provide boiler test water as follows:

"P" alkalinity = 200 ppm
residual silica = 20 ppm, added as sodium metasilicate
residual phosphate = 20 ppm, added as sodium dihydrogen phosphate
residual sulfite = 20 ppm, added as sodium sulfite
calcium hardness = 10 ppm, added as calcium chloride
magnesium hardness = 5 ppm, added as magnesium sulfate
cycles of concentration = 15 ppm
O_2 level after N_2 sparging = 0.25-0.5 ppm

The boiler was energized and allowed to come to equilibrium overnight at 100 psig. On the second through fifth days two sets of samples (each set consisted of a steam sample and a blowdown sample) were taken per pressure step at a minimum of one hour and a maximum of one and a half hours between sets (at a given pressure). The samples, refrigerated during the accumulation stage in glass containers, were then analyzed using standard gas chromatographic procedures under the following conditions:

G.C. unit: Perkin Elmer Model 990
Detector(s): Thermal conductivity or flame ionization
Column Size: 6' x 2 mm id Pyrex
Packing: 14% Carbowax 20 M/2% KOH on 80/100 mesh Supelcoport
Oven Temperature: 110°C
Carrier Gas: N_2 at 20 ml/min at 40 psig
Sample Size: 1 μl
Injection Temperature: 105°C.

The resulting distribution ratios, calculated according to equation (I), are reported below in Table 1. Also reported are the dissociation constants, pK_b, for the materials tested.

TABLE 1
DR VALUES AT VARIOUS PRESSURES

Compound	Pressure (psig)	DR	pK_b
Morpholine	0	0.4	5.7
	100	1.0	
	200	1.6	
	300	1.4	
	400	1.2	
	500	1.2	
	600	1.3	
	700	1.2	
	900	1.3	
	1100	1.3	
	1300	1.3	
	1450	1.2	
aminomethylpropanol	0	0.1	4.18
	100	0.5	
	200	1.0	
	300	0.8	
	400	0.8	
	500	0.9	
	600	0.8	
	700	0.8	
	900	0.9	
	1100	0.9	
	1300	0.9	
	1450	0.9	

TABLE 1 (Continued)

Compound	Pressure (psig)	DR	pK_b
cyclohexylamine	0	2	3.4
	100	9.3	
	200	23	
	300	20	
	400	8.0	
	500	6.7	
	600	6.6	
	700	6.1	
	900	5.3	
	1100	4.7	
	1300	4.4	
	1450	4.1	
ammonia	0	10.0	4.75
	100	7.1	
	200	7.1	
	300	6.3	
	400	5.0	
	500	5.3	
	600	4.2	
	700	4.2	
	900	3.9	
	1100	3.6	
	1300	3.4	
	1450	1.6	

Example 2

An investigation was undertaken to determine the possible effects, if any, of boiler chemicals or water quality on DR. The testing method used was similar to that reported in Example 1. In the present test, however, water "P" alkalinity was increased by a factor of two; and in the comparative "without chemical" tests, the hardness, phosphates and silicates were removed completely. Some results of these tests are reported below in Table 2 in terms of comparative average DR values with chemicals and without chemicals. All DR's reported are averages of at least two to nine separate data points.

TABLE 2

EFFECT OF BOILER CHEMICALS OR WATER
QUALITY ON DISTRIBUTION RATIO

Compound	Pressure	Average DR With Chemicals	Average DR Without Chemicals
morpholine	400	1.3	1.0
	700	1.2	1.2
	1450	1.2	1.4
cyclohexylamine	400	7.9	8.3
	700	5.8	7.1
	1450	3.8	5.0
aminomethylpropanol	400	0.9	0.7
	700	0.8	0.8
	1450	0.9	1.1

The results of Table 2 are seen to indicate that over the pressure range of interest, with respect to practicing the present invention, no significant effect on DR was noted due to either the absence of boiler chemicals or an increase in alkalinity.

Example 3

Also investigated was the effect, if any, of increased neutralizing amine concentration on the various DR's. This was accomplished by simply doubling the amine concentration from 50 ppm to 100 ppm and comparing the results. A testing method similar to that reported in Example 1 was used. The amines tested were morpholine and cyclohexylamine. The results of these tests are reported below in Table 3 in terms of comparative average DR at 50 ppm and 100 ppm.

TABLE 3

EFFECT OF AMINE CONCENTRATION ON DR

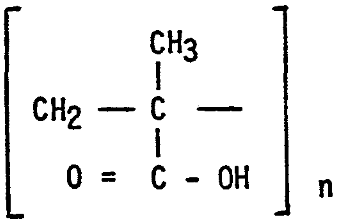
Compound	Pressure (psig)	Average DR at 50 ppm	Average DR at 100 ppm
morpholine	400	1.2	1.2
	500	1.2	1.2
	600	1.3	1.4
	700	1.2	1.3
	900	1.3	1.3
	1100	1.3	1.3
	1300	1.3	1.2
	1450	1.3	1.2
cyclohexylamine	400	8.2	7.3
	500	6.6	7.0
	600	6.4	7.2
	700	5.9	6.6
	900	5.2	5.6
	1100	4.7	4.7
	1300	4.6	4.0
	1450	4.1	4.3

Based on the results from Table 3, there is seen to be no significant effect of amine concentration on the DR. Of course, the individual values for quantity of amine present in the steam and blowdown samples increased significantly, but the magnitude of the DR still remained about the same.

MAKING AMINE-NEUTRALIZED ORGANIC ACID

Example 4

This example is seen to illustrate the preparation of an aqueous solution of alpha amine-neutralized organic acid to be used in accordance with the present invention. The starting material was polymethacrylic acid (PMA) having the formula:



$$\left[CH_2 - \overset{\displaystyle CH_3}{\underset{\displaystyle O = C - OH}{C}} - \right]_n$$

which polymer had a molecular weight average of 6,000 to 12,000 as determined by gel permeation chromatography, using as reference a commercial sodium polymethacrylate of advertised molecular weight of 8,000-10,000.

A stock solution is made by the following procedure:

1. weigh out 250 g of tap water (pH = 8.2)
2. add 65 g of PMA (30.8% actives)
3. mix well
4. record pH and neutralize to desired pH with amine

At this point, the 4% PMA solution is reweighed and the amount of amine used is recorded. The solution is brought to a final weight of 500 g and a final pH reading is taken. The tap water added increased the pH by about .2 units.

The weights of the amine used to reach various pH's for numerous solutions actually made were as follows:

Solution 1: 4% PMA stock solution, 500 g total weight, pH about 2.5

Solution 2: Solution 1 neutralized to pH = 7 with 17.5 g of morpholine; final pH = 7.2

Solution 3: Solution 1 neutralized to pH = 7 with 18.0 g of AMP; final pH = 7.1

Solution 4: Solution 1 neutralized to pH = 7 with 17.2 g of cyclohexylamine; final pH = 7.0

Solution 5: Solution 1 neutralized to pH = 9.5 with 211.3 g of morpholine; final pH = 9.7 (this solution less than 4% PMA)

Solution 6: Solution 1 neutralized to pH = 10 with 25.5 g of AMP; final pH = 10.0

Solution 7: Solution 1 neutralized to pH = 7 with 15.5 g of morpholine, then to pH = 10.8 with 59.7 g of AMP; final pH = 10.9

Solution 8: Solution 1 neutralized to pH = 7 with 18.2 g of morpholine, then to pH = 10.9 with 53.7 g of cyclohexylamine; final pH = 11.1

Solution 9: Solution 1 neutralized to pH = 7 with 18.4 g of morpholine, then to pH = 9.8 with 46.8 g of AMP; final pH = 10.1

Solution 10: Solution 1 neutralized to pH = 7 with 19.0 g of morpholine to pH = 9 with 11.1 g of AMP, then to pH = 11 with 37.9 g of cyclohexylamine; final pH = 11.0

Solution 11: Solution 1 neutralized to pH = 7 with 24.1 g of morpholine, to pH = 9 with 15.3 g of AMP, then to pH = 11 with 8.9 g of sodium hydroxide anhydrous; final pH = 11.5

Solution 12: Solution 1 neutralized to pH = 8 with 21.2 g of morpholine; final pH = 8.0

Solution 13: Solution 1 neutralized to pH = 7.5 with 22 g of AMP; final pH = 8.0

Solution 14: Solution 1 neutralized to pH = 8 with 20.9 g of cyclohexylamine; final pH = 8.1

Example 5

This example is seen to further illustrate the preparation of an aqueous solution of alpha amine-neutralized organic acid to be used in accordance with the present invention. The starting material was Acrysol A - 41, commercially available from Rohm and Haas. It is a copolymer of methacrylic and acrylic acid, having a molecular weight average of about 10,000-12,000 and a mole ratio of methacrylic acid to acrylic acid of about 9:1.

A stock solution is made according to the same procedural steps set forth in the preceding example, however, (71.5 g of) Acrysol A-41 (28% actives) was used instead of the PMA.

The weights of the amine used to reach various pH's for numerous solutions actually made were as follows:

Solution 1: 4% copolymer stock solution, 500 g total weight, pH about 2.65

Solution 2: Solution 1 neutralized to pH = 7 with 19.3 g of morpholine; final pH = 7.2

Solution 3: Solution 1 neutralized to pH = 7 with 20.2 g of AMP; final pH = 7.2

Solution 4: Solution 1 neutralized to pH = 7 with 23 g of cyclohexylamine; final pH = 7.6

Solution 5: Solution 1 neutralized to pH = 9.2 with 129.6 g of morpholine; final pH = 9.4 (not stable at this pH)

Solution 6: Solution 1 neutralized to pH = 10 with 43.6 g of AMP; final pH = 10.2

Solution 7: Solution 1 neutralized to pH = 10 with 35.5 g of cyclohexylamine; final pH = 10.1

Solution 8: Solution 1 neutralized to pH = 7 with 21.7 g of morpholine, then to pH = 9 with 13.6 g of AMP, then to pH = 10.8 with 114 g of cyclohexylamine; final pH = 11.1

EFFICACY OF TREATMENT IN BOILER

Example 6

A series of tests were conducted to determine the efficacy of alpha amine-neutralized organic acids as boiler water treatments. The tests were conducted in the research boiler described in Example 1 and schematically illustrated in Figure 3. As already noted, certain boilers are highly susceptible to caustic corrosion as a result of iron oxide deposits formed on interior surfaces. Thus, any treatment which will prevent the formation of iron oxide deposits is considered to be a highly desirable supplement for a coordinated phosphate/pH control program.

Since the research boiler was electrically powered using immersion heating probes, deposits formed directly on probe surfaces. On completion of the tests, the deposits formed on the heating probes were analyzed to determine the quantity of iron oxide present and the total amount of deposit.

During the tests performed, boiler conditions included a coordinated phosphate/pH control program, 15 cycles of concentration, operating pressure of 1450 psig, 3.4 ppm Fe^{+2} contaminated feedwater, and boiler probes of differing heat flux values. One probe had a heat flux value of 240,000 BTU/ft^2/hr; while the other had a heat flux of 185,000 BTU/ft^2/hr. Test durations were 2 days.

The feedwater had the following composition:

7.5	ppm $NaHCO_3$
0.04	ppm Silica
8.2	ppm Tri-sodium phosphate
0.2	ppm antifoam (polyalkylene glycol)
6	ppm $NaNO_3$ (for conductivity)
16.7	ppm $FeSO_4$ (3.4 ppm Fe)

The tests included comparative studies of alpha amine-neutralized polymeric acid dispersants with commonly used polymeric acid dispersants as sodium salts. The materials tested were as follows:

Comparative Product X: Commercial sodium polymethacrylate, reported molecular weight = 6,000-8,000

Comparative Product Y: Commercial sodium polymethacrylate, reported molecular weight = 8,000-10,000

Product A: Polymeric acid starting material of Example 5, neutralized with AMP, pH = 10.0, stored at 120°F for three months before testing

Product B: Polymeric acid starting material of Example 5, neutralized with morpholine, pH = 8.0, stored at 120°F for three months before testing

Product C: Polymeric acid starting material of Example 4, neutralized with morpholine and AMP, pH = 10.3, stored at 120°F for three months before testing

Product D: Polymeric acid starting material of Example 4, neutralized with morpholine, pH = 8.1, stored at 120°F for three months before testing

The results of these tests are reported below in Table 4 in terms of amount of iron deposition (in g/ft^2) on the probes.

TABLE 4

EFFICACY IN BOILER

Treatment	Dosage (ppm polymer)	pH Range	Residual PO_4 (ppm)	240,000 BTU/ft^2/hr.		185,000 BTU/ft^2/hr.	
				Fe as Fe_2O_3	Total	Fe as Fe_2O_3	Total
None	-	6.3-10.5	15	2.94	5.68	2.53	5.00
None	-	9.4-10.4	35	2.86	3.84	2.64	3.88
None	-	8.5- 8.8	35	0.88	2.13	1.32	2.25
Product X	20	9.4-10.4	35	0.92	1.29	1.03	1.27
Product Y	20	10.1-10.7	35	1.04	1.63	0.47	0.62
Product A	20	10.2-10.3	40	0.40	1.22	0.29	0.67
Product B	20	9.8-10.2	38	0.48	1.00	0.61	0.96
Product C	20	9.4- 9.9	25	0.41	0.94	0.23	0.57
Product D	20	9.6- 9.8	25	0.21	0.72	0.12	0.43

Based on the results reported in Table 4, not only are treatments according to the present invention considered to be efficacious for boiler water, but they are seen to compare favorably with treatments containing the sodium salts of the organic acids. Accordingly, the coordinated phosphate/pH corrosion control treatment can be supplemented with an organic acid treatment in a form which will neither adversely affect the critical Na:PO_4 nor increase the solids level in the boiler water.

It should be kept in mind that the stronger the basicity of the alpha amine neutralizing agent, the less amine required to neutralize the polymeric acid dispersant. To avoid problems related to fungi growth, higher pH formulations, e.g., above 8.5, are preferred.

A preferred supplemental treatment composition for use with the coordinated phosphate/pH corrosion control treatment is Solution 1 of Example 5 neutralized to pH = 8.5 with 27.3 grams of morpholine.

Having thus described the invention, what is claimed is:

CLAIMS

1. A coordinated phosphate/pH corrosion control method for the treatment of boiler water, in which residual orthophosphate is maintained in the water in an amount of from about 1 to about 50 ppm and a Na:PO_4 of from about 2:1 to less than 3:1 is maintained in the water, characterised by, supplementing the treatment with an effective amount for the purpose of an aqueous solution of alpha amine-neutralized organic acid.

2. A method as claimed in claim 1, characterised in that the organic acid is at least one member selected from the group consisting of carboxylic acid polymer, sulfonic acid polymer, phosphonic acid polymer and poly phosphonic acid.

3. A method as claimed in claim 2, characterised in that the organic acid is carboxylic acid polymer.

4. A method as claimed in claim 3, characterised in that the organic acid is selected from the group consisting of acrylic acid polymer and methacrylic acid polymer.

5. A method as claimed in claim 4, characterised in that the organic acid is copolymer of acrylic acid and methacrylic acid.

6. A method as claimed in claim 5, characterised in that the organic acid is polymethacrylic acid.

7. A method as claimed in any one of the preceding claims, characterised in that the "alpha" amine is at least one member selected from the group consisting of morpholine, cyclohexylamine and aminomethylpropanol.

8. A method as claimed in any one of the preceding claims, characterised in that the organic acid is added in an amount of from about 1 to 150 ppm.

9. A method as claimed in claim 8, characterised in that the organic acid is added in an amount of from about 5 to about 50 ppm.

10. A method as claimed in any one of the

preceding claims, characterised in that the Na:PO_4 is maintained at from about 2.13:1 to about 2.85:1.

11. A method according to claim 10, wherein the Na:PO_4 is maintained at from about 2.2:1 to about 2.6:1.

12. A method as claimed in any one of the preceding claims, characterised in that the residual orthophosphate level is maintained at from about 2 to about 30 ppm.

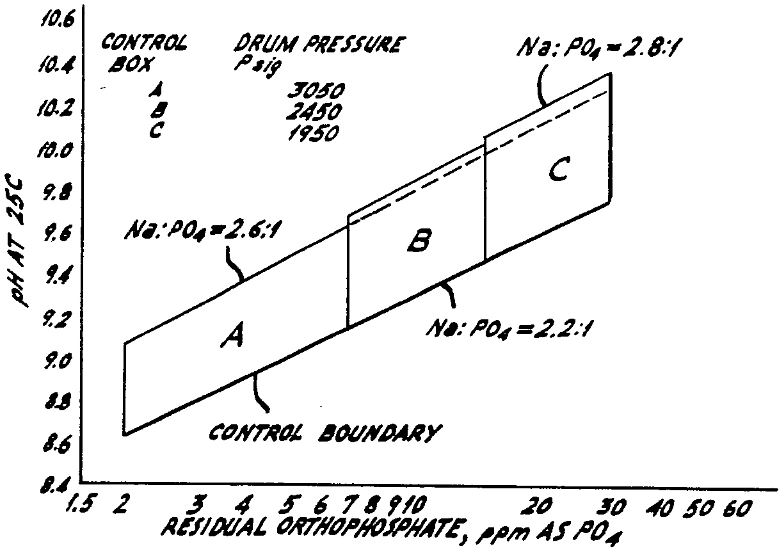
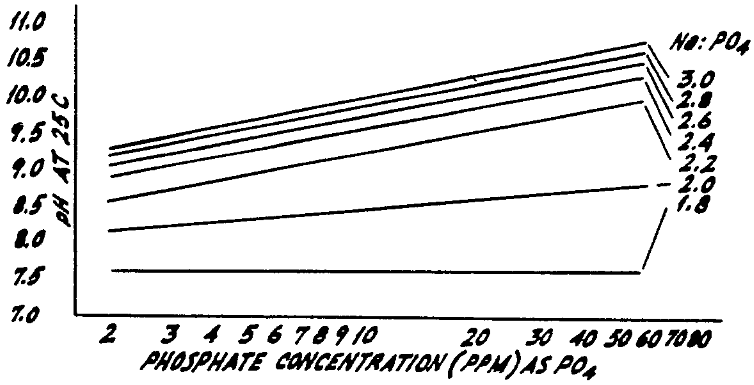


FIG. 1.

FIG. 2.



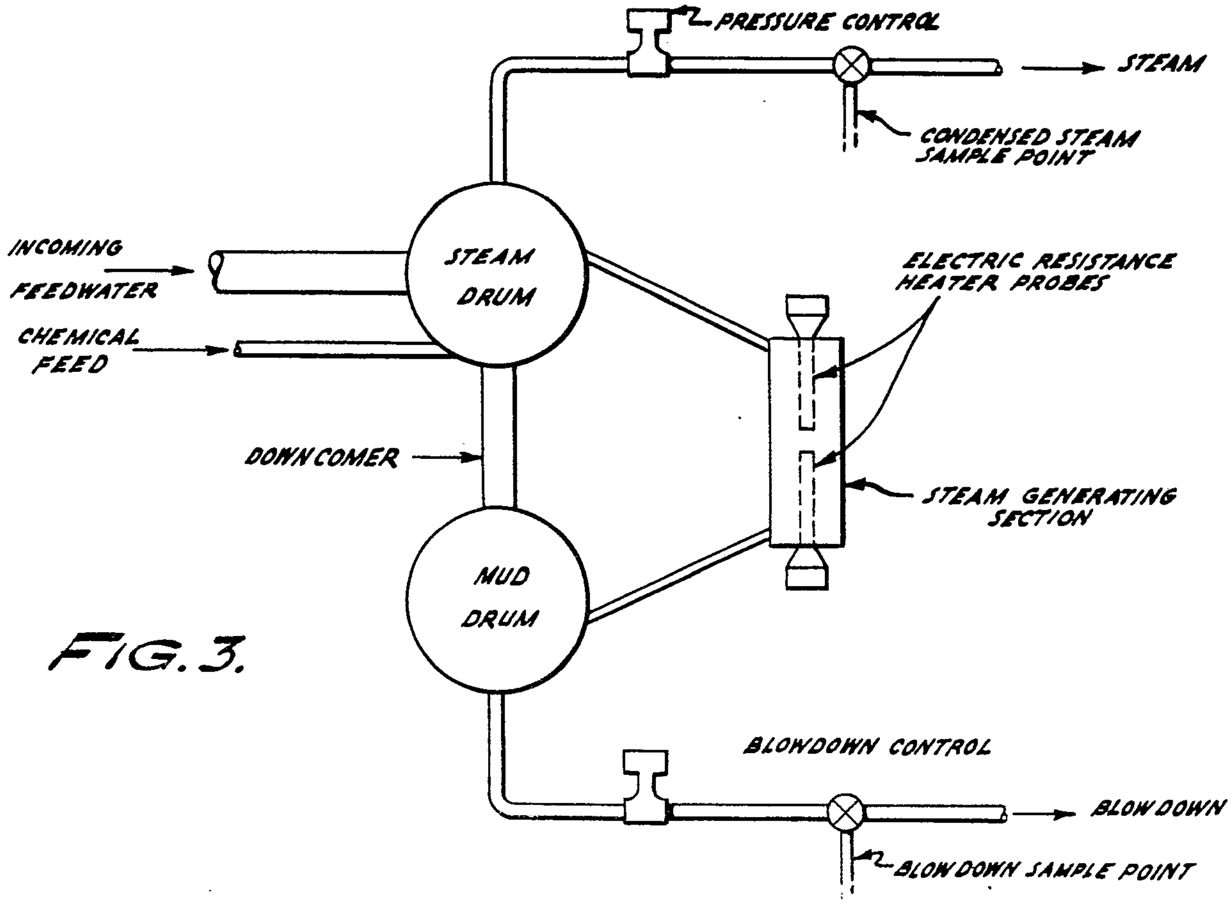


FIG. 3.

European Patent
Office

EUROPEAN SEARCH REPORT

0018083

Application number
EP 80 30 0809

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	GB - A - 860 958 (I.C.I.)	
A	FR - A - 2 192 192 (BETZ LABOR)	
A	FR - A - 2 246 620 (DREW CHEMICAL) ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl. ^{3})

C 23 F 11/08

TECHNICAL FIELDS SEARCHED (Int.Cl. ^{3})

C 23 F 11/08
11/10
11/12
11/14

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

☒ The present search report has been drawn up for all claims

Place of search THE HAGUE	Date of completion of the search 23-07-1980	Examiner TORFS

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